

## Using Synchrotron FTIR Microspectroscopy To Study The Interaction Between Uranium and Atmospheric Corrosion Products on Steel

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**Introduction:** Atmospheric corrosion products found on iron include  $\text{Fe}(\text{OH})_3$ ,  $\text{Fe}(\text{OH})_2$ ,  $\alpha\text{-FeOOH}$ ,  $\gamma\text{-FeOOH}$ ,  $\delta\text{-FeOOH}$ ,  $\text{Fe}_3\text{O}_4$ , ferrihydrite, and  $\gamma\text{-Fe}_2\text{O}_3$ .<sup>1-4</sup> Researchers have found that the type of oxide formed, its crystallinity, particle size depend on the corrosion conditions, but most have observed that the first solid corrosion product that is formed is  $\gamma\text{-FeOOH}$ , which converts to  $\alpha\text{-FeOOH}$  and  $\gamma\text{-Fe}_2\text{O}_3$ .<sup>1-3</sup> These corrosion products crack easily and allow more corrosion to occur.<sup>4</sup> The amorphous oxyhydroxide ( $\delta\text{-FeOOH}$ ) also forms on the surface of low alloy steel, which act as a protective barrier during atmospheric corrosion. Very little has been published concerning the interaction of uranium with corrosion products on steel. Payne found that ferrihydrite transformation to crystalline minerals reduce the adsorption of uranium from solution.<sup>5</sup> In previous work, co-precipitation of uranium with synthesized corrosion oxides and oxyhydroxides (magnetite, maghemite, lepidocrocite, goethite and ferrihydrite) indicate hexavalent  $\text{O}=\text{U}=\text{O}$  asymmetric stretching ( $\sim 900\text{ cm}^{-1}$ ).

**Methods and Materials:** Low carbon steel coupons (1010) were obtained from a structural sheet steel supplier (Fleischer Steel of Bay Shore, New York) and were sheared into 6x6 inch sections, deburred, cleaned thoroughly with Alconox<sup>TM</sup> detergent to remove oils and rinsed in doubly-distilled water. Uranyl nitrate stock solution (400 mM) was prepared by dissolving 202 g of  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Analar, BDH Chemicals Ltd., Poole, England) in one liter of deionized water. To obtain 10 and 40 mM of uranyl nitrate solution, the stock solution was diluted. The coupons that underwent humidity treatment were placed in a custom-made Plexiglas<sup>TM</sup> box, which uses a blower and humidifier containing distilled water to create and maintain a relative humidity of  $>90\%$  at room temperature. Wet/dry cycles were conducted on a 12-hour basis. Citric acid cleaning treatment involved immersing the coupons in 0.1 M citric acid solution for 20 hours, allowing it to air-dry and then transferred to a 0.05 M hydrogen peroxide solution. Following treatment with peroxide the sample was dried and placed in fresh 0.1 M citric acid solution. The coupon was finally rinsed two times in deionized water and air dried. Treatments were conducted for one minute and air-dried for five minutes.

**Results:** Corroded and non-corroded 1010 carbon steel surfaces with and without exposure to 40 mM uranyl nitrate were analyzed using synchrotron-based Fourier Transform Infrared (FTIR) spectroscopy and microspectroscopy. This data indicates that the uranium exists in a hexavalent state following exposure to a lightly corroded or non-corroded surface and when incorporated onto a heavily corroded steel surface. FTIR data indicates that surface uranium contamination is primarily associated with areas that have large amounts of hydroxides (Figure 1 and 2) and trapped nitrate compounds. FTIR analysis indicate a large OH stretch at  $3000\text{ cm}^{-1}$ , a nitrate peak at  $1415\text{ cm}^{-1}$  and  $\text{O}=\text{U}=\text{O}$  asymmetric stretching at  $934\text{ cm}^{-1}$ . The  $\text{O}=\text{U}=\text{O}$  stretching frequency is lower than that of uranyl nitrate ( $951\text{ cm}^{-1}$ ), suggesting a change in U-O bonding. A cross-section of the corrosion product layers in a sample that was cyclically exposed to 10 mM uranyl nitrate solution and rusted indicate that goethite, which has characteristic peaks at  $890$  and  $790\text{ cm}^{-1}$ , is found underneath the lepidocrocite, which has a characteristic peak at  $1020\text{ cm}^{-1}$ . This indicates that lepidocrocite is the first corrosion product to be formed, which later converts to goethite (Figure 3). The samples were subsequently cleaned in a citric acid solution, and both the surfaces and the solution were analyzed. ICP-AES indicate that the heavily corroded steel surfaces adsorb more than the lightly corroded sample, giving further proof that the uranium accumulates in thick corrosion layers where removal is incomplete. FTIR showed that the decontamination treatment removed uranium and most of the corrosion products (no presence of  $1020\text{ cm}^{-1}$  peak nor  $890$  and  $790\text{ cm}^{-1}$  peaks were found that would indicate lepidocrocite or goethite) from the surface. Residual carboxylate salts, which have peaks at  $1400$  and  $1700\text{ cm}^{-1}$  were also found on the surface using FTIR.

**Conclusions:** Corrosion products formed on 1010 carbon steel are composed of an upper layer of oxyhydroxides. Uranium seems to be found in occluded, hydroxide-rich areas. The uranium may also still be associated with the nitrate in the bulk or in areas where nitrate salts are present. Citric acid was found to effectively chelate and remove uranium from lightly corroded surfaces, but some uranium may still be retained in heavily corroded areas. Residual citrates found on the surface after decontamination treatment may further hinder corrosion.

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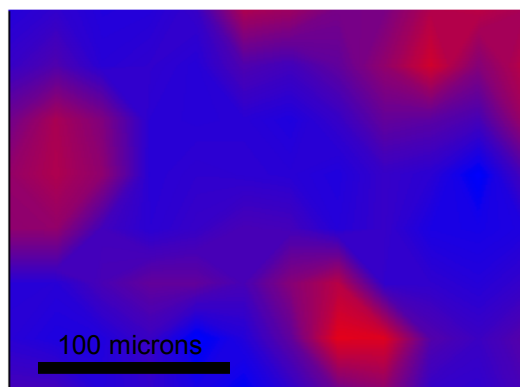


Figure 1: FTIR Maps of a sample exposed to 40 mM of uranyl nitrate solution and dried in air, showing O=U=O stretching (left) and O-H stretching (right).

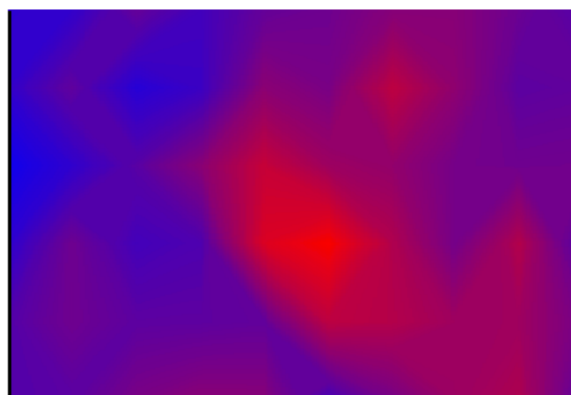
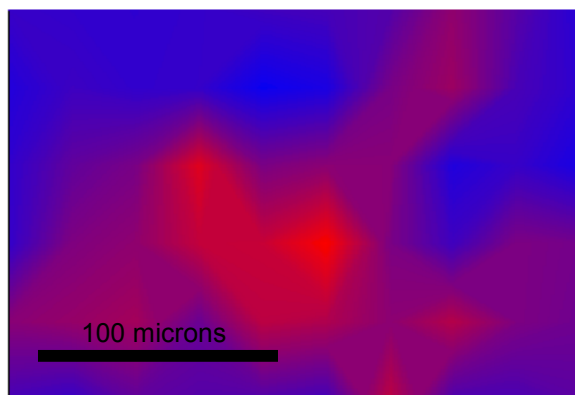


Figure 1: FTIR Maps of a sample exposed to 40 mM of uranyl nitrate solution and placed in humidity chamber, showing O=U=O stretching (left) and O-H stretching (right).

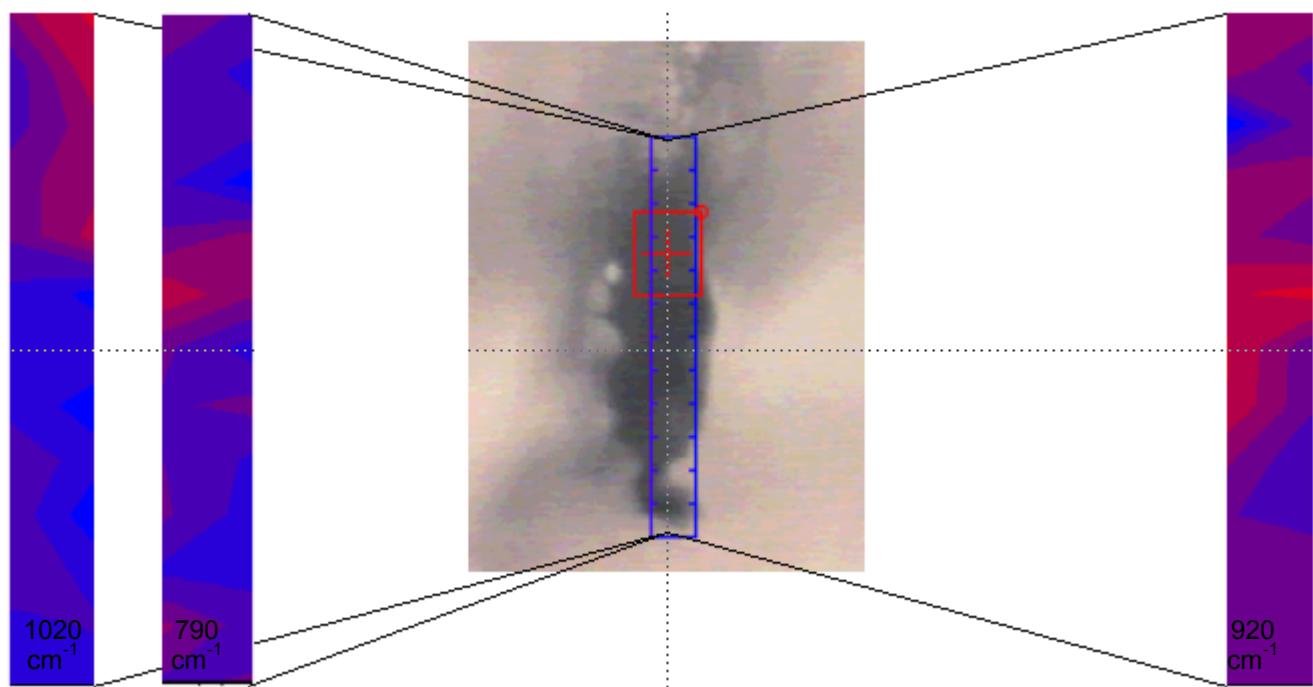


Figure 3: Microtomed E/R/E/R sample show lepidocrocite layer (a) over goethite layer (b) and O=U=O stretching (c).